APB 11/25/69

UNITED STATES DEPARTMENT OF AGRICULTURE

FOREST SERVICE

c/o Fenhann/FHS TRN 02110

COMBUSTIBILITY OF PLANT MATERIALS: The Pyrolysis of the Components of Western Cottonwood

Final Report
Cooperative Agreement No. 12-11-204-1
Supplement Number 17

by

F. Shafizadeh
C. Philpot
G. McGinnis

June 10, 1969

TO: U.S. DEPARTMENT OF AGRICULTURE--FOREST SERVICE
INTERMOUNTAIN FOREST AND RANGE EXPERIMENT STATION
NORTHERN FOREST FIRE LABORATORY
MISSOULA, MONTANA

FROM: WOOD CHEMISTRY LABORATORIES
UNIVERSITY OF MONTANA
SCHOOL OF FORESTRY AND DEPARTMENT OF CHEMISTRY
MISSOULA, MONTANA

6200-7 (6/65)

U.S. GOVERNMENT PRINTING OFFICE : 1965 O—777-887

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I. INTRODUCTION

Plant material or natural fuel is simply a combination of chemical compounds which break down under thermal stress to produce the volatile compounds which support combustion. Therefore, it is important to know the chemical makeup of plants, their pyrolysis products, and the interaction between components. Thus, a cooperative agreement was initiated between this laboratory and the Northern Forest Fire Laboratory to complement fuel chemistry, moisture, physical properties and ignition studies in that laboratory.

Specifically, this work deals with:

1. Isolating the major components of a model fuel.
2. Identification of the pyrolysis products of these components.
3. Thermally analyzing the components by differential thermal analysis and thermogravimetric analysis.
4. Estimating the relative flammability of each component.

This work has progressed well ahead of schedule and we were therefore able to proceed with preliminary work into the mechanisms of xylan pyrolysis and the pyrolysis characteristics of leveglucosan.

II. ISOLATION OF THE MAJOR COMPONENTS OF BLACK COTTONWOOD

Cottonwood was chosen as the model fuel because it contains only one major hemicellulose, 4-O- methyl glucoronoxylan. This greatly simplified the work with the hemicellulose component. Cottonwood is also a potentially commercial western hardwood, the chemistry of which is little known. Therefore, our data will be useful from a utilization as well as a fire research standpoint.

The cottonwood was ground to 40-60 mesh in a Wiley Mill and extracted in a modified Soxhlet extractor with ethanol-benzene for 4 hours followed by 95 percent ethanol for 4 hours (Browning 1967). The meal was then extracted with cold water for 3 hours. The wood was deliquified with sodium chlorite and acetic acid following the procedure of Wise (1945). The resulting holocellulose was fractionated by the methods of Timell (1961) to provide cellulose and xylan (fig. 1). The amount of lignin was determined by the Klason method (1906). Milled wood lignin

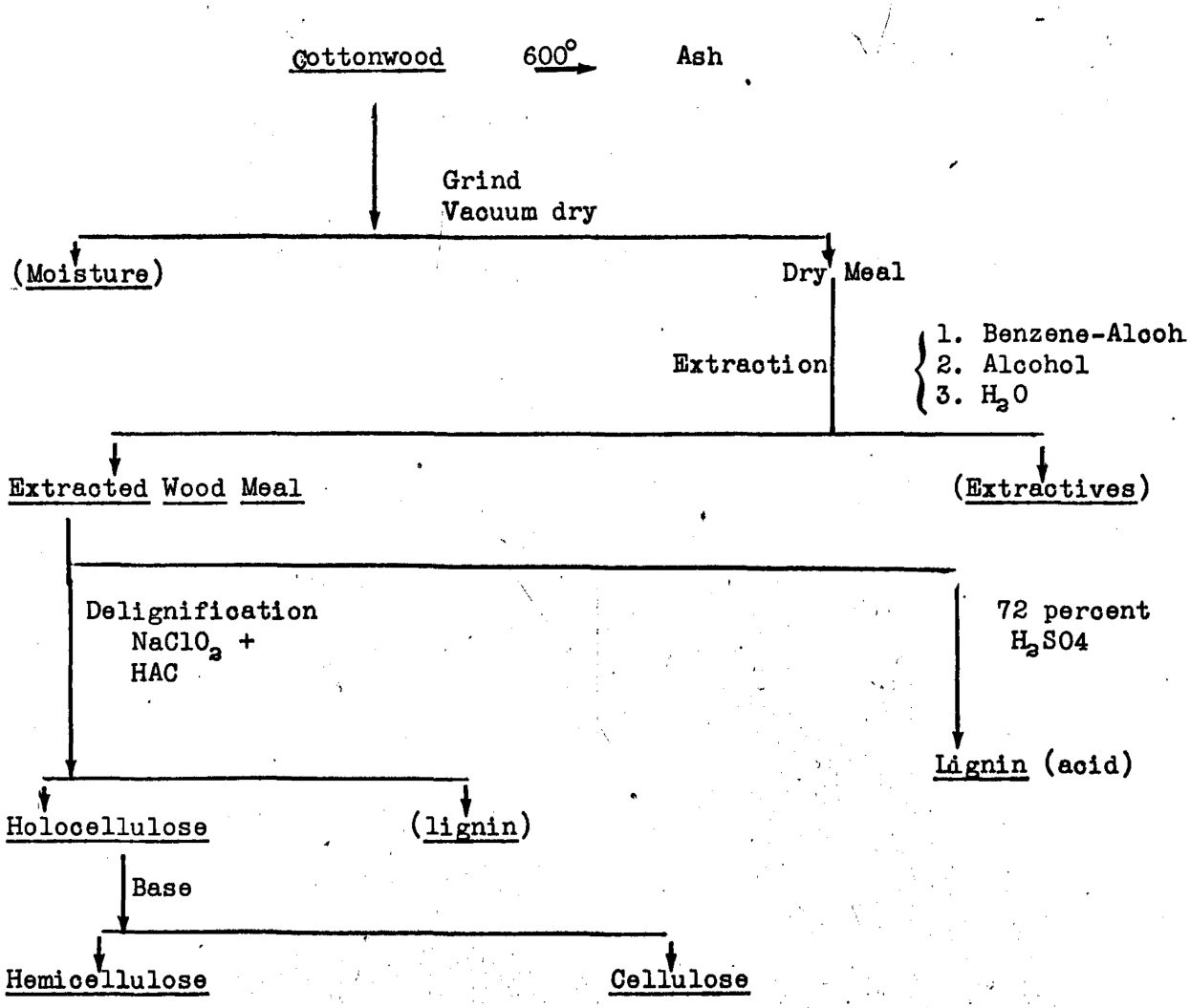

Figure 1.--Scheme of component isolation.

from eastern cottonwood was used for the thermal analysis because it is much less degraded (Sarkanen 1963). This material was obtained from an outside source.[1] The percent composition of cottonwood is shown in table 1 and 2.

The cell wall polysaccharides (holocellulose component) was hydrolyzed to the sugars and indicated the presence of cellulose, "xylan" and trace amounts of "mannan". Those polysaccharides were isolated by alkaline extraction. This gave 58.4 percent cellulose, 23.3 percent 4-O- methylglucurono xylan and 6.63 percent glucomannan based on the holocellulose.

The holocellulose fraction was also extracted with methyl sulfoxide to give a small yield of O-acetyl-4-O methylglucuronoxylan. This was used for the determination of acetly groups, which are hydrolyzed under the alkaline condition of the systematic fractionation. Analysis of this product showed 9.87 percent acetyl content.

Hydrolysis of the "xylan" and analysis of the hydrolyzate showed the presence of D-xylose and only a trace of D-glucose impurities. However, as usual, no 4-O-methyl-D-glucuronic acid was detected. The presence of this component was ascertained through methoxyl determination of 4-O-methylglucurono-xylan. This gave a value of 16.3 percent in the acetylated product. On the basis of these data, the O-acetyl-4-O-methylglucurono-xylan component contains an average of one uronic acid for each nine D-xylose units and about half of the D xylose units contain an acetyl group.

Assuming that on hydrolysis of the cell wall polysaccharides all the D-xylose is derived from acetyl-4-O-methylglucoronoxylan and the D-mannose is derived from the glucomannan fractions, the percentage of each polysaccharide may be calculated as shown in table 3.

All these components were vacuum dried and their mineral contents determined. The total ash content was determined by ignition. Flame photometry was used for calcium, potassium, and sodium determination. Iron and phosphorus were determined by colorimetry following wet digestion (table 4).

III. THE THERMAL ANALYSIS OF THE COMPONENTS

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) are used to determine the temperature at which a compound begins to pyrolyze, the rate of pyrolysis, and the amount remaining after active pyrolysis. The occurrence of endo-and exothermic processes and their intensity can also be observed. DTA and TGA were carried out on each of the components of cottonwood to assess the contribution of each component to the combustion process.

Ten mg. of material were used for TGA. The heating rate was 15°/min. in a nitrogen atmosphere. The same heating rate and atmosphere was used on the DTA with 15 mg. of fuel. All experiments were from 25° to 500°C.

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[1] Sarkanen, K.V. is located at the Univ. of Wash. at Seattle.

Table 1.--Chemical composition of black cottonwood

	Dry weight
	Percent
Holocellulose	73.8
Cellulose	43.1
Hemicellulose	
Xylan	17.3
Glucomannan	4.9
Acid Lignin	31.0
Extractives	2.0
Ash	0.37

Table 2.-- Composition of the woody tissues of *Populus trichocorpa*

Component	Dry wood	Extracted wood
	Percent	Percent
Benzene-alcohol (2:1) soluble	4.65	
Alcohol soluble	.51	
Water soluble		
TOTAL EXTRACTIVES		5.16
Klason lignin		27.7
Cell wall polysaccharides		73.89

Table 3.-- Cell wall polysaccharides

Polysaccharide	Holocellulose	Wood
	Percent	Percent
Cellulose	58.4	43.1
Acetyl-4-O-methylglucuronoxylan	23.4	17.3
Glucomannan	6.63	4.99

Table 4.--Mineral content of black cottonwood components

	Ash	Ca	K	P	Fe	Na
Wood	.37	.059	.065	.0122	.0074	.006
Extracted wood	.29	.058	.016	.0006	.0057	.006
Holocellulose	1.02	.020	.001	.0014	.0032	.394*
Cellulose	.15	.002	.002	.0003	.0063	.003
Xylan	1.68	.024	.007	.017	.008	.205*

*Additions due to base extraction procedure.

Xylan was by far the least thermally stable of the three components. It began to lose weight at about 215°. An endotherm occurs at this time showing depolymerization or some other breakdown. Rapid weight loss continues until about 325°, at which time a definite rate change occurs. The residue at 450° was about 6 to 8 percent. (figs. 2 and 3)

Cellulose began to pyrolyze at about 315° and decomposed much more rapidly than xylan. The residue at 450° was 6 percent. Acid lignin was quite thermally stable. Although it began to degrade at about 200°, more than 60 percent of the material remained as a residue at 450°. The rate of weight loss was very slow compared to the carbohydrates. Since acid lignin is somewhat degraded by the isolation procedure, milled wood lignin from the same genus was used as a more representative material. This was less thermally stable, but still lost 50 percent of its weight by 450°(table 5).

The DTA of each component is reflected in the DTA of the wood (fig. 3). The chromatograms of the pyrolyzates from the components were also additive. Therefore, it appears that studying each component of fuel is a valid and practical approach to studying the whole fuel.

IV. IDENTIFICATION OF THE PYROLYSIS PRODUCTS OF CELLULOSE AND XYLAN

Since the carbohydrates appear to be responsible for the majority of the flammable volatiles, the project was focused on the investigation of cellulose and xylan. The pyrolysis products from birch lignin have been identified by Kitao as high molecular weight compounds (Kitao and Watenabe 1968).

This work coupled with our thermal analysis, shows lignin to be far less important than the carbohydrates in terms of combustion.

Most of the carbohydrate work has been with xylan because it is the first component to break down and very little was known about its pyrolysis. Originally levoglucosan, a primary intermediate, was used as a model compound for cellulose and much work was done in identifying its pyrolysis products (Shafizadeh, et.al. 1968; Ostojic 1968).

We used two types of furnaces for these studies. One was a modified Sargent Micro Combustion Apparatus. This system allowed to use samples up to 2 grams, so that large quantities of products could be collected for further analysis and identification. A series of condensers downstream from the furnace allowed fractional collection of the volatiles and tar. The char remained in the boat which could be weighed. These products were then subjected to various tests, such as gas-liquid chromatography, thin-layer chromatography, mass spectroscopy, infrared spectroscopy and other chemical tests. This system could be run under vacuum with a stream of nitrogen.

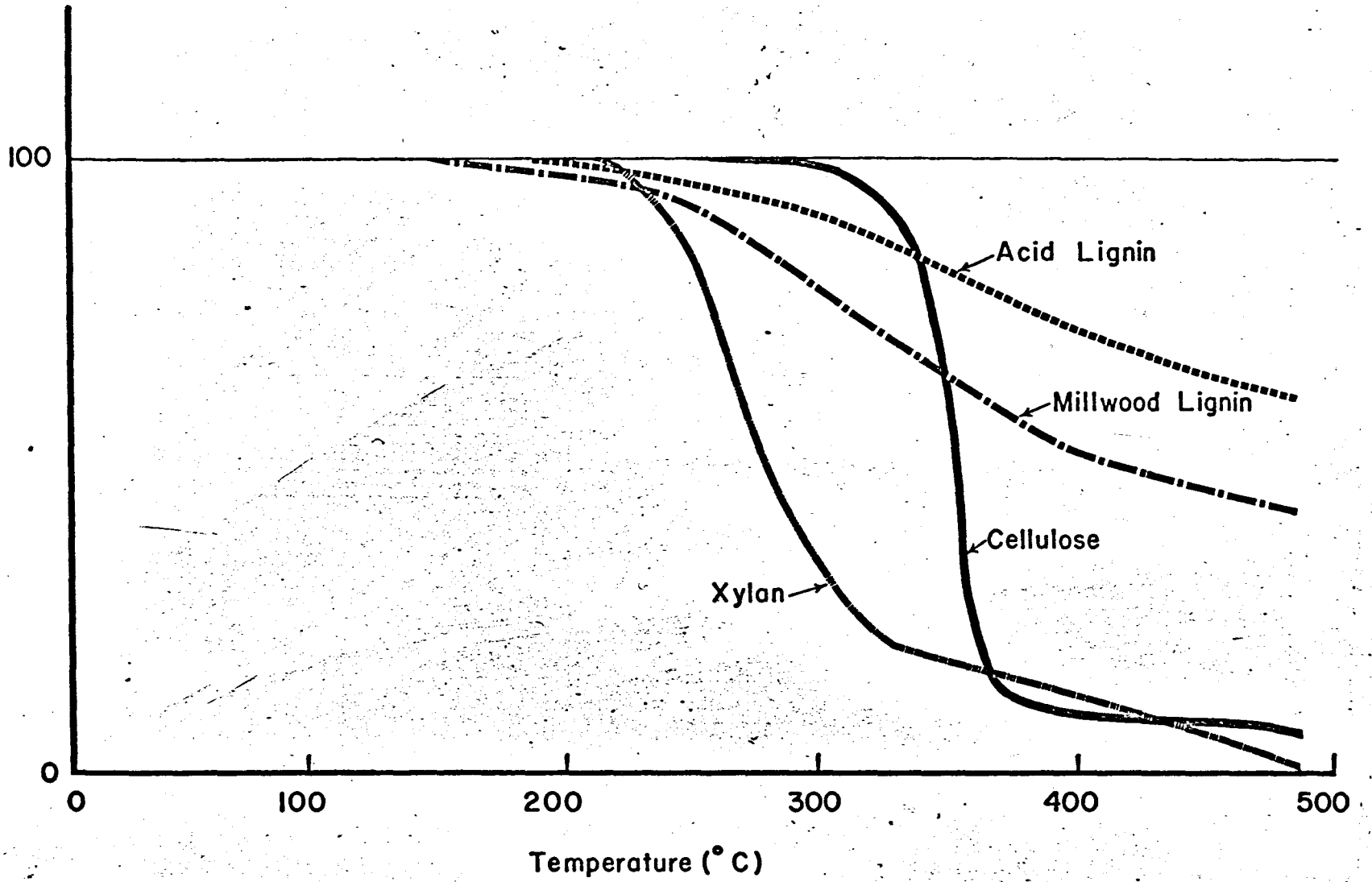


Figure 2.--The TGA of cottonwood and its components.

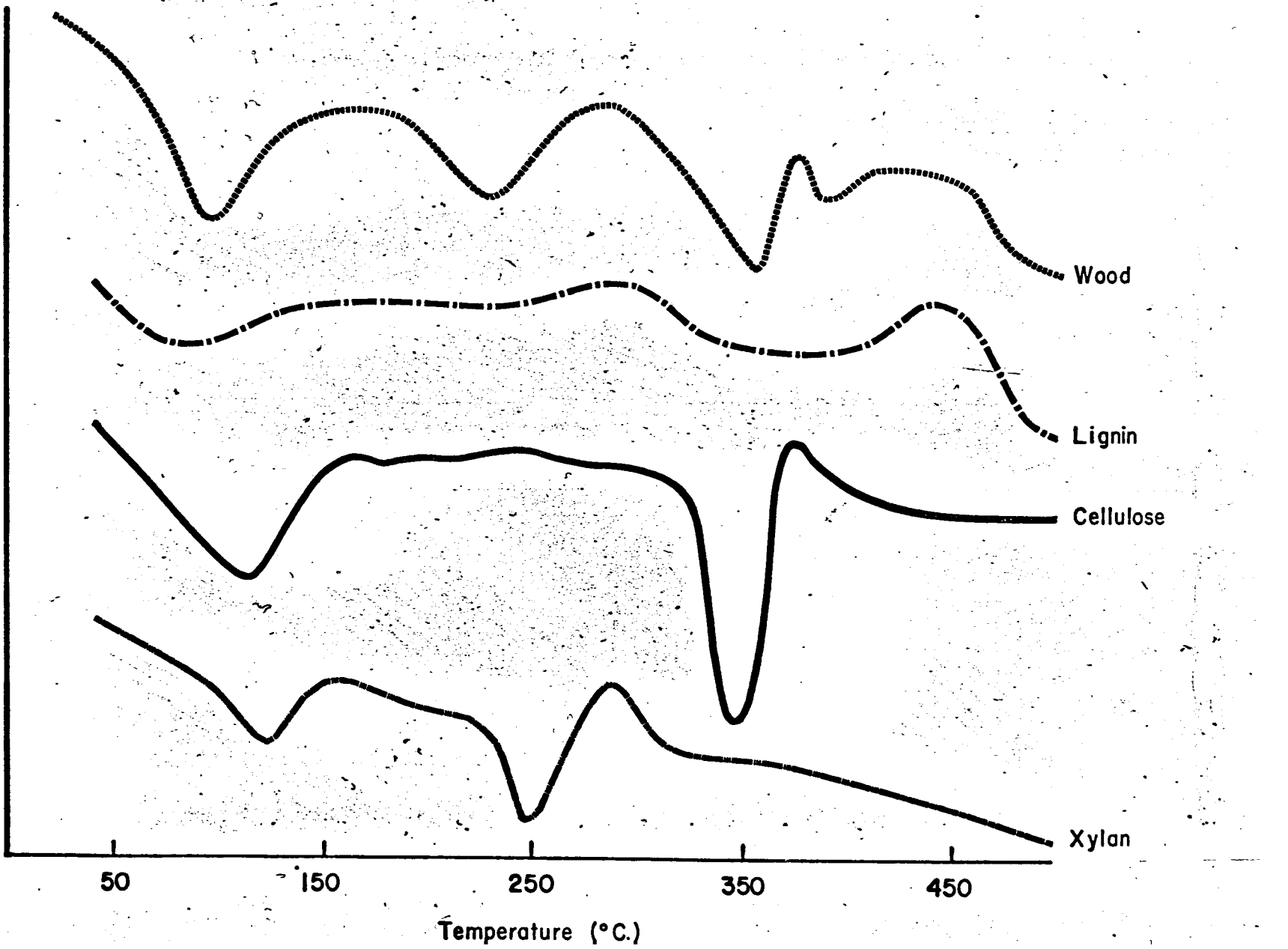


Figure.--The DTA of cottonwood and its components.

Table 5.--The pyrolysis characteristics of cottonwood components

Compound	Temperature of initiation (°C)	Maximum Rate of Pyro (mg./°C)	Residue at 450° Percent
Wood	175	*	19
Cellulose	320	.25	6
Xylan	215	.11	6
Milled wood lignin	175	.03	45
Acid lignin	200	.02	60

*Wood exhibits two definite rates, one during xylan pyrolysis and the other during cellulose pyrolysis.

The second pyrolysis system consisted of a modified Perkin-Elmer unit connected directly into the carrier gas stream of a F and M model 5750 temperature programed gas chromatograph. This system allowed identification of the volatile products directly without collection or trapping once calibration was achieved. Usually only 15-20 mg. of material were used in this unit.

The peaks on the chromatograms were identified by splitting the stream from GLC and collecting the individual products in capillary tubes immersed in liquid nitrogen or dry ice and acetone. The carbonyl compounds were collected as 2,4-dinitrophenylhydrazones. Thin-layer chromatography was used to identify the 2,4-dinitrophenylhydrazone derivatives. The procedures of Byrne were generally followed (1969). The identification of most of the compounds was verified by mass spectroscopy.

Figure 4 provides a comparison between the gas chromatograms of the volatile products derived from cellulose and levoglucosan. In these chromatograms, the peaks represent the following: (1) noncondensable gases, (2) acetaldehyde, (3) furan, (4) acrolein, (5) methanol, (7) butanedione, (8) crotonaldehyde, (10) pyruvaldehyde, (13) hydroxyacetone, (14) glyoxal, (15) acetic acid, (17) furfural, (18) formic acid, and (20) 5-methyl furfural. This shows that the thermal degradation products of cellulose and levoglucosan, although closely similar, are not quantatively identical. Cellulose provides more glyoxal and less furfural (a dehydration product) as compared to levoglucosan.

The char, water, and CO_2 from the pyrolysis of cellulose are shown in table 6. The char from cellulose amounted to 6 percent and contained 25 percent H, 76 percent C, and 21.5 percent O. The tar was found to be mostly levoglucosan by previous authors (Madorsky, et. al. 1958).

Our data on the pyrolysis of xylan seem to fit the general pattern that has been outlined for cellulose (Shafizadeh 1969). Pyrolysis of xylan runs parallel to that of D-xylose and provides some tar and volatile compounds. The tar contains a polymeric material that can be separated by gel fillration chromatography. This is apparently formed from the pyrolysis products and can be hydrolyzed to give a high yield of D-xylose.

The composition of the volatile products separated by gas chromatography is shown in figure 5. They are (1) fixed gases, (3) furan, (4) acetone/propionaldehyde, (5) methanol, (6) crotenaldehyde, (7) glyoxal, (8) acetic acid, and (9) furfural. The products vary quantatively between extraction procedures. The yield of char, tar, and volatiles was 6, 34, and 44 percent, respectively. However, this ratio changed greatly with experimental conditions such as amount of starting material and temperature range.

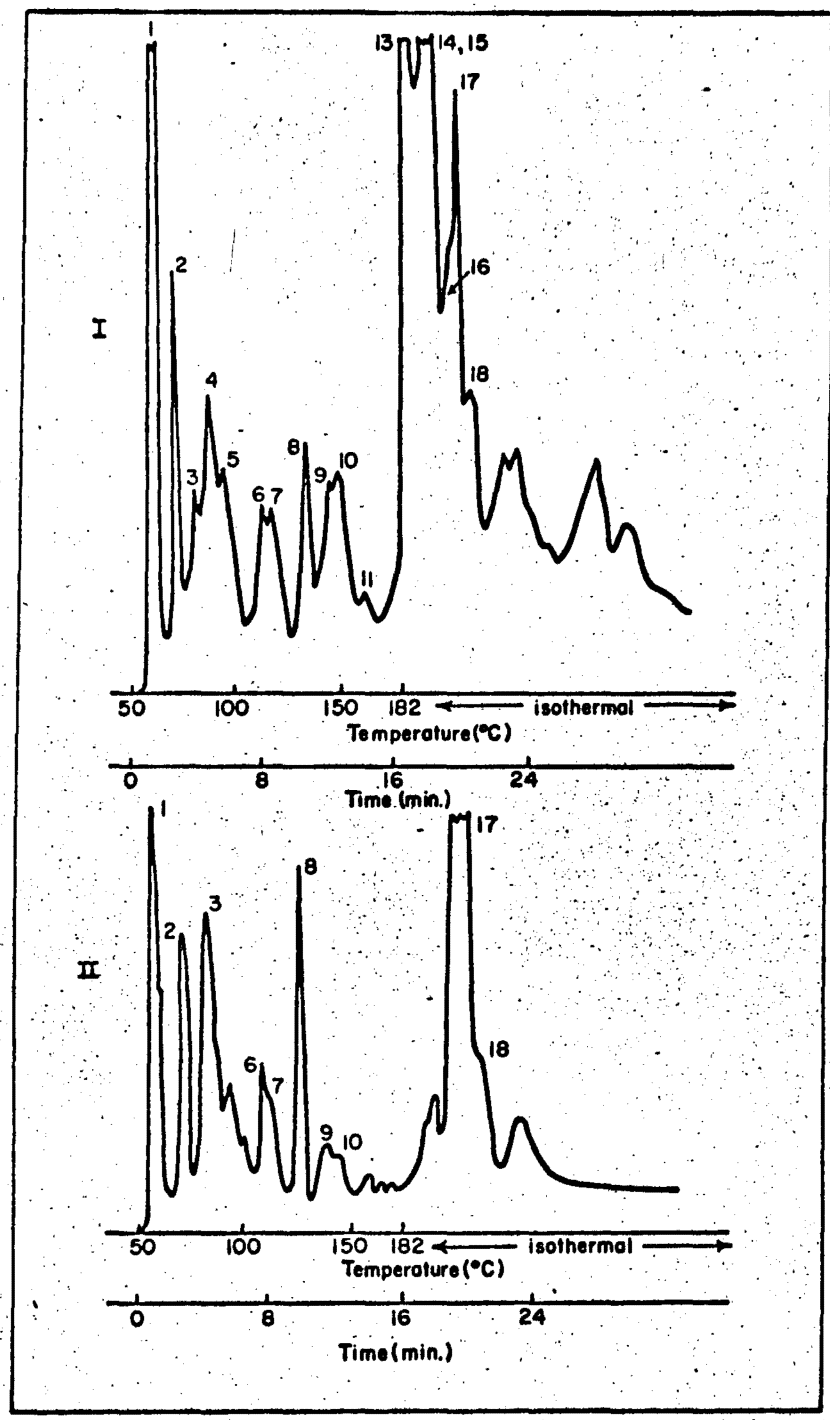


Figure 4.--Chromatograms of cellulose (I) and cellulose treated with $ZnCl_2$ (II).

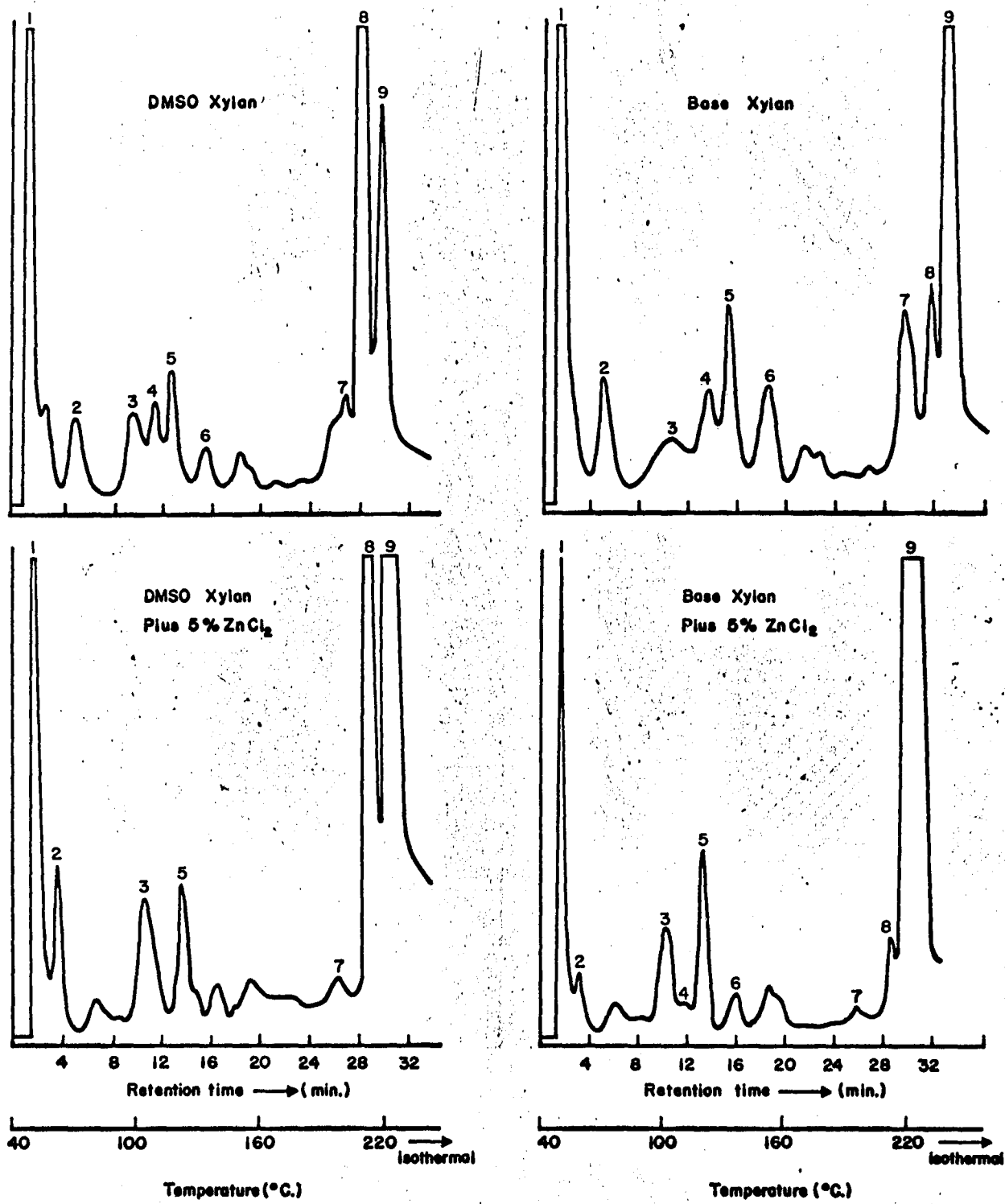


Figure 5.--The gas chromatograms of xylan extracted with DMSO or base, ~~and treated with zinc chloride.~~

Table 6.--The effects of $ZnCl_2$ on carbohydrate pyrolysis

	Ti (°C)	Rate (mg./°C)	Residue	H_2O	CO_2	Furfura
			Percent			
Cellulose	320	.25	6	**5	-	.8
Cellulose + $ZnCl_2$	220	.05	38	**20	-	2.0
Xylan*	215	.11	6	6.7	6.7	1.8
Xylan + $ZnCl_2$	175	.06	25	21.1	7.1	5.1
Levoglucosan	210	.10	6	8.7	2.9	.9
Levoglucosan + $ZnCl_2$	180	.04	40	20.1	6.8	3.0
Wood	220	-	19	-	-	-
Wood + $ZnCl_2$	175	-	40	-	-	-

*Base extracted
**Estimation

V. EFFECTS OF AN ACID SALT ON THE PYROLYSIS OF LEVOGLUCOSAN, CELLULOSE AND XYLAN

The net effect of various salts and flame retardants is well documented; however, the mechanisms are still a mystery. As a continuation of the work described thus far, the products from the pyrolysis of carbohydrates treated with ethanolic solution of $ZnCl_2$ were analyzed. The results indicate possible mechanisms which are currently being tested by using model compounds.

The effects of $ZnCl_2$ on cellulose, xylan, and levoglucosan are quite similar. (figs. 6,7, and 8) In summary these are:

A. A decrease in the temperature at which pyrolysis begins.

B. A decrease in the rate of pyrolysis under dynamic heating.

C. An increase in the char, H_2O, and furfural at the expense of the two and three carbon fragments, especially glyoxal.

VI. SUMMARY AND CONCLUSIONS

The results of the study show:

1. The major components of wood pyrolyzed independently and each component can be studied separately to the number of variables.

2. Xylan (hemicellulose) is the first component to pyrolyze. Its rate of pyrolysis is slower than cellulose, (probably due to the lower temperature), but it is nearly completely pyrolyzed prior to the initiation of cellulose pyrolysis.

3. Cellulose and hemicellulose produce the same general products upon pyrolysis. These constitute the bulk of the volatile products from wood.

4. Lignin is the least important component of wood with respect to volatilization and flaming combustion.

5. The effect of an acid salt on pyrolysis of xylan, cellulose, and levoglucosan is to lower the intiation temperature, decrease pyrolysis rate, increase char, H_2O, and furan compounds.

This work has laid a foundation for further integrated research into the mechanisms of pyrolysis, effects of catalysts and the relationships between fuel chemistry and ignition, rate of spread, and intensity of fire. It has provided new information about the hemicellulose component, which with cellulose forms about 70 percent of the wood and the major amount of the volatile combustible materials.

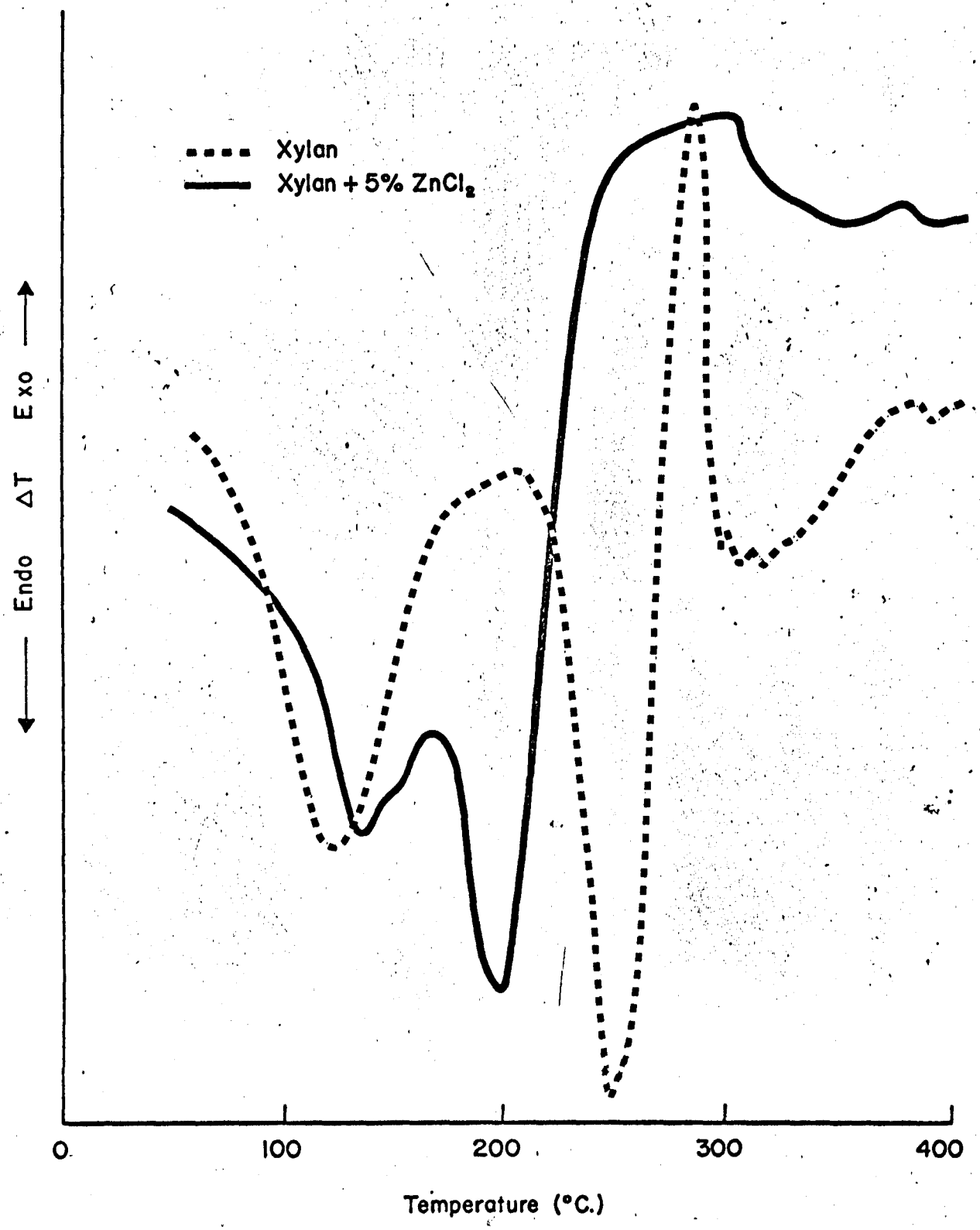
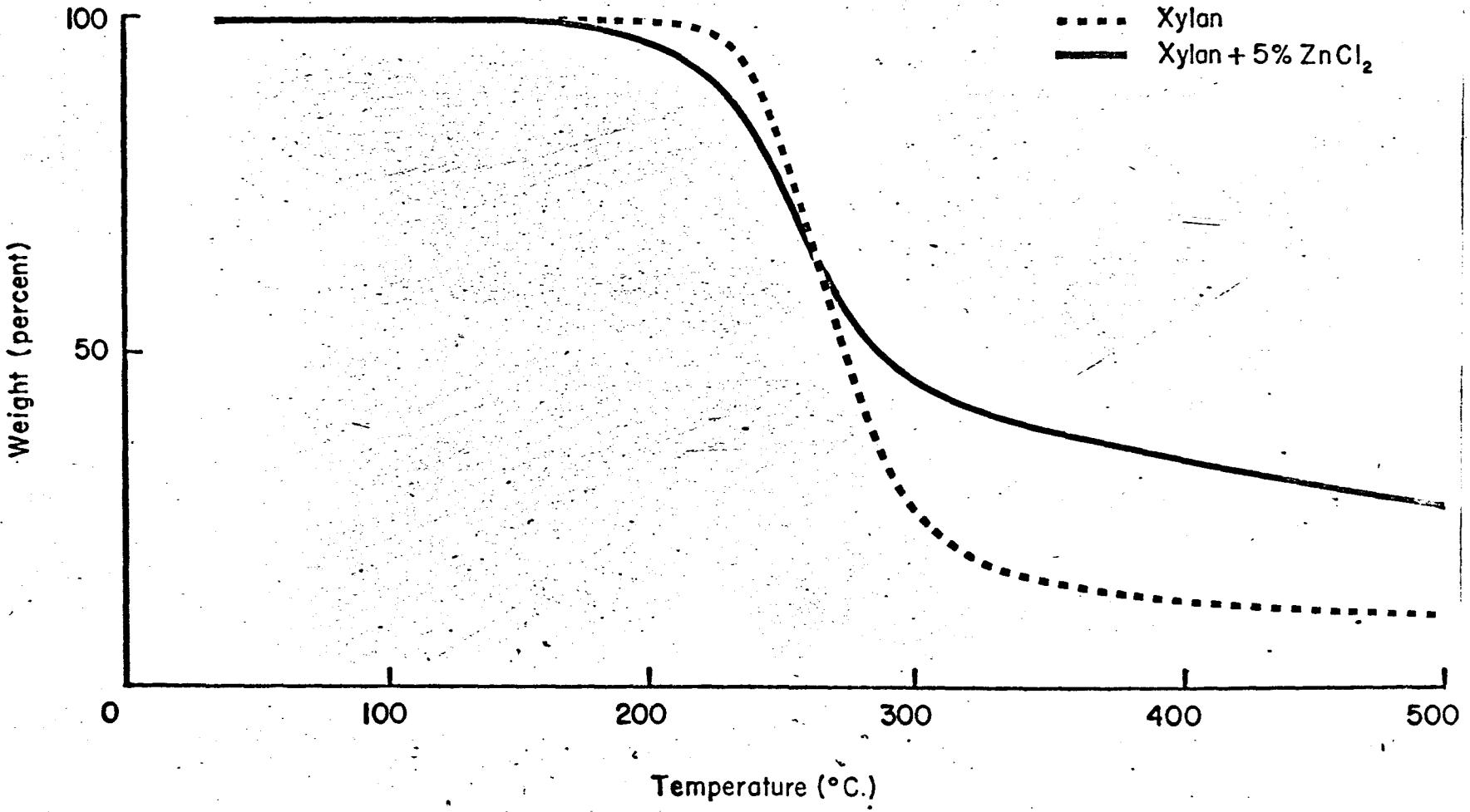


Figure 6.--The DTA of xylan and xylan treated with $ZnCl_2$.



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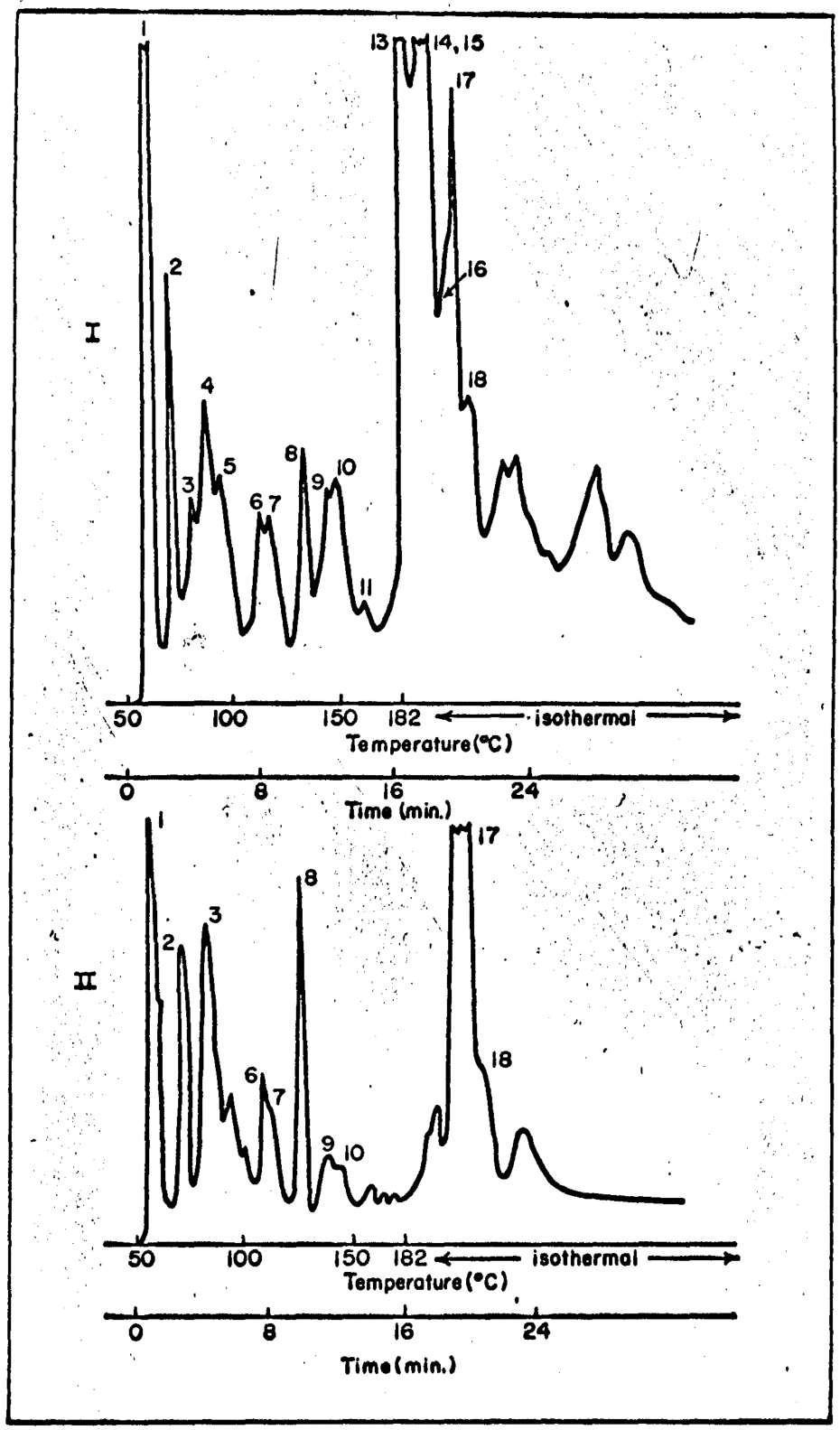

Figure 8.-- Gas chromatograms of pyrolyzates from cellulose(I) and cellulose treated with 10% zinc chloride(II) (with flame ionization detector).

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